

UNIQUE CONTINUOUS PROCESS HARDWARE: AN EXAMPLE OF FLOW CHEMISTRY AS AN EMERGING FIELD IN CHEMICAL INDUSTRIES

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ABSTRACT

The basic theme of the present research is to provide a guideline for carrying out the heterogeneous reactions like reactive precipitation in a continuous manner with maximum efficiency to set an example of flow chemistry which is the emerging field under consideration in chemical industries. Reactive precipitation is generally used for the treatment waste streams generating from chemical or nuclear industries. Ion exchange is necessary for carrying out the precipitation and such types of reactions are instantaneous and controlled by equilibrium limitations and mixing efficiency. Calcium, magnesium, sodium or nuclear elements generally present in the waste stream in their nitrate form and these nitrates can be converted into their oxalates by carrying out the reactive precipitation. The objective of the present research work is to design the process hardware which is capable for synthesizing the oxalate of above mentioned elements in a continuous manner efficiently. The designed process hardware should not reach the criticality limit through all aspects if it is implemented as such in nuclear industries also. Optimization of the process parameters have been arrived at by employing the system containing calcium in its nitrate form. From the experimental studies the typical reaction kinetics was obtained and it was observed that reaction takes place in two stages with 75 % conversion in 1st stage in 10 seconds and remaining 25 % takes nearly about further 900 seconds in 2nd stage. The rate of reaction in 2nd stage is substantially lower and it is considered as rate controlling stage. If these both stages carried out in a single reactor on a continuous basis then the rate of reaction in the 1st stage reduces drastically due to the reduction in the collision frequency between the ions and the equilibrium limitations going to establish in the dissociation of reactants entering the reactor system along with fresh incoming feed.

By taken such a typical type of obtained reaction kinetics and above mentioned technical issues into consideration, the continuous process hardware for synthesizing 52 kg of calcium oxalate per day has been designed, fabricated, characterized, validated experimentally and correlated with the theoretically predicted results.

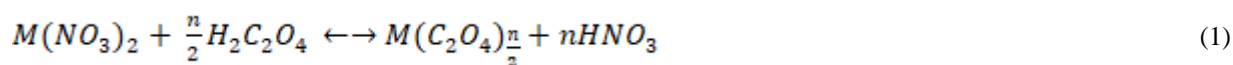
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1. INTRODUCTION

The waste streams generating from chemical industries generally contain hazardous chemicals and need to be neutralised or removed before it can be safely reintroduced into the environment otherwise it causes damage to human health and/or the environment. Chemical methods generally used for the treatment of hazardous waste include ion exchange, precipitation, oxidation and reduction and neutralization etc. Most of the waste streams generating from the nuclear or chemical industries contain heavy metal ions in their nitrate form. Several methods exist to remove these nitrates of the elements like calcium, magnesium, sodium or the nuclear elements to their oxides and one of them is the chemical precipitation of these elements in the form of their respective oxalates and subsequent calcinations converting them into their oxides. Chemical precipitation involves a chemical reaction in

which separable solid particulate matter get form either by changing the properties of the solution in order to reduce the solubility of contaminant or by forming an insoluble substance through a chemical reaction. Reactive precipitation is in current practice for the treatment of radioactive waste generating from nuclear industries. The waste stream generating from the Purex process contains uranium and plutonium ions and these can be separated from it by carrying out reactive precipitation. Optimization of the geometric parameters and the kinetics of the reactive precipitation between aqueous nitrates of these elements and oxalic acid is essential for the process design of such a system. The objective of the work is to design and optimize a system for precipitating out the oxalate of calcium via the reactive precipitation between its nitrate and oxalic acid. Calcium, sodium and magnesium nitrate dissociates into their respective ions. Similarly, oxalic acid dissociates into hydrogen and oxalate ions. Calcium/Magnesium/Sodium ions combines with oxalate ions and produces their respective oxalates while hydrogen ions reacts with nitric ions and produces nitric acid as a byproduct. The reaction scheme between the nitrates of calcium/magnesium/sodium and oxalic acid has been shown as follow:



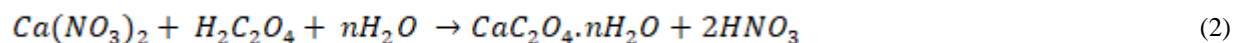
Where, M is the calcium/magnesium/sodium.

It is just an ion exchange reaction and hence it is an instantaneous type of reaction. The rate of such reactions depends upon the concentration of reactants, mixing efficiency and the rate of dissociation of reactants and formed products into the reaction mixture. The byproduct in the selected reaction scheme is a nitric acid and it is very strong as compared to oxalic acid and hence it remains completely in the dissociate form and retards the dissociation of comparatively weak oxalic acid due to common ion effect given by hydrogen ions. Similarly, it also affects the dissociation of calcium/magnesium/sodium nitrate due to the common ion effect given by nitric ions. Therefore, it is also necessary to achieve maximum conversion of the reactants so as the residual unreacted concentration of such elements in the discarded material should be minimum. Because of these two major reasons, determining the kinetics of reactive precipitation between the nitrate of calcium/magnesium/sodium and oxalic acid becomes a major challenge for chemical industries in order to optimize the parameters to carry out such a reaction with maximum efficiency(Escher, et al., 2005). Because of the equilibrium limitations to carry out such reactions in a minimum volume with as possible as less energy consumption and on a continuous basis is a challenging task for chemical industries. Cost associated with the processes generally used in the treatment of waste streams affects the overall economy of industry and therefore the industrial sector in developing countries dispose the waste directly to the environment without proper treatment. Therefore, the goal of the present research is to set an example for the treatment of such waste streams with less energy and manpower consumption by carrying out such processes on a continuous basis.

2. SELECTION OF AN APPROPRIATE SYSTEM

Ion exchange type of reaction depends on the extent of dissociations of reactants and its present concentrations in the liquid phase. Reaction between oxalic acid and calcium nitrate, or magnesium nitrate or sodium nitrate produces oxalates of calcium, magnesium and sodium respectively. Out of these, only calcium oxalate has a negligible solubility in the reaction mixture containing reaction by-product nitric acid. Solubility of calcium, sodium and magnesium oxalate in water is 6.7mg/L, 37000mg/L and 380 mg/L respectively(Haynes, 2012-2013.). Due to the lowest solubility of calcium oxalate in the reaction mixture, it practically does not affect the kinetics of the ion exchange type of reaction. Sodium oxalate and magnesium oxalate are having higher solubility in aq. Media. Therefore, these oxalates are almost in their dissociate form.

These dissociated ions retards the dissociation of their nitrates into the reaction mixture due to common ion effect and the reaction system becomes complex. Therefore, for simplicity calcium nitrate has been chosen for the case study. Hence, from the aforementioned systems, calcium nitrate and oxalic acid has been chosen for the formation of calcium oxalate and the reaction scheme to be studied in this work is represented as follow:



3. PRELIMINARY STUDIES

Preliminary studies were carried out to arrive at the optimum range of parameters which can be used to obtain, a) Complete conversion and the form of calcium oxalate precipitated out b) Excess of oxalic acid was needed to obtain complete conversion of calcium nitrate in a specified time in order to estimate the processing capacity of the designed system.

3.1 Reaction Kinetics

3.1.1 Thermo-Gravimetric Analysis (TGA)

The conversion obtained in the reaction can be estimated on the basis of the obtained yield of hydrated calcium oxalate solid product. Prior to this it was necessary to find out the hydrated state of calcium oxalate formed and hence TGA study was carried out to investigate the form of calcium oxalate whether it is in mono- or di- hydrate state which is necessary to set the complete material balance.

Calcium nitrate tetra hydrate and oxalic acid di hydrate were procured from Merck (India) Ltd, Mumbai and used for the synthesis of hydrated calcium oxalate as such.

The instrument DTG-60H was used for thermo-gravimetric analysis. Nitrogen gas was used for purging. The heating rate of TGA instrument was 10°C/min. The temperature range under which TGA study has been carried out was from room temperature (~30°C) to 500°C. Experimental Set-up as shown in Figure-1, was used for carrying out the reactive precipitation between calcium nitrate and oxalic acid for the synthesis of the hydrated calcium oxalate. Diameter of the reactor (T) chosen was 0.115m and was of the same height. Diameter of the pitched blade stirrer (D), width of the baffle (W) and the location of the stirrer from the bottom of the reactor (h) is equal to $\frac{T}{3}$, $\frac{T}{12}$ and $\frac{T}{3}$ respectively and is as per the recommended standard design of the stirred contactor (McCabe, et al., 1993). The geometric details are given in Table-1.

The vessel of 650 ml has been chosen to study the kinetics of the reactive precipitation between calcium nitrate and oxalic acid.

3.1.2 Ethylene Di-Amine Tetra Acetic acid (EDTA) Titration

EDTA titration has been carried out to investigate the concentration of residual calcium present in the dissolved state in the reaction mixture in order to validate the conversion estimated on the basis of obtained yield of hydrated calcium oxalate solid product and to find out the reaction kinetics. Same experimental set-up as shown in Figure-1 was used for carrying out the reaction between calcium nitrate and oxalic acid in order to estimate the reaction kinetics by following the standard EDTA titration method (Khopkar, 1998). Disodium salt of ethylene di amine tetra acetic acid (EDTA), ammonia buffer solution of pH 10 and Erio-chrome Black T indicator required for EDTA titration were procured from SD. Fine-Chem.Pvt. Ltd. (Mumbai, India).

4 RESULTS AND DISCUSSIONS

4.1 TGA Analysis

Thermogravimetric analysis (TGA) is useful to investigate the hydrated state of the formed calcium oxalate (Stuart, 2002). The obtained TGA analysis graph for the calcium oxalate hydrate has been shown in Figure-2 and from this study it was observed that the first decomposition peak was obtained at 150°C and second at 500°C and it is in concurrence with the TGA of the standard monohydrate of calcium oxalate (Vlaev, et al., 2008.). Hence, it was concluded that the calcium oxalate formed in the process has been obtained as monohydrate in nature. The conversion obtained has been estimated on the basis of the obtained yield of the monohydrate calcium oxalate and the complete set of material balance has been shown in Table-2. The effect of excess amount of oxalic acid on the conversion has been shown in Figure-3 which shows that 50% of excess oxalic acid by wt. is optimum for achieving 98-99% (quantitative) conversion of calcium nitrate to calcium oxalate over the reaction period of 15 minutes. As the percentage of excess oxalic acid increases the obtained yield of calcium oxalate monohydrate also increases and this is due to the following reasons:

Even though calcium oxalate is sparingly soluble in water, some small amounts of calcium oxalate dissolves due to the more acidic condition generated by the presence of reaction by-product nitric acid. This dissolved amount gets dissociated into the reaction mixture as follow:



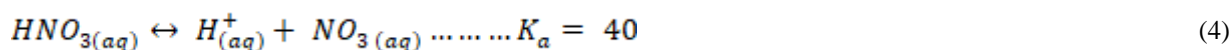
Since the dissociation constant of oxalic acid is significantly higher than that of the calcium oxalate and according to Le Chatelier's principle the amount of oxalic acid presents in excess retards the dissociation of dissolved calcium oxalate. Therefore more and more calcium oxalate gets precipitated out and finally results into increasing the yield of monohydrate calcium oxalate obtained. The excess (un-reacted) oxalic acid solution can be recovered after the filtration of the solid calcium oxalate to wash the solid reaction product to avoid any future contamination or can be recycled and supplemented with fresh oxalic acid for the next set of reaction.

4.2 Validation of the Extent of Conversion by Carrying Out Titration of Calcium with Ethylene Di-Amine Tetra-Acetic Acid (EDTA)

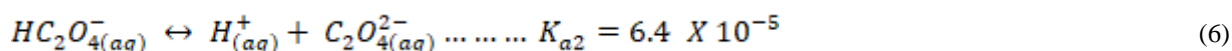
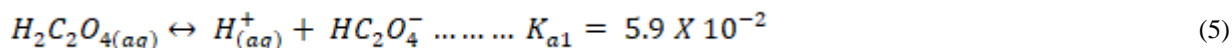
EDTA titration detects the concentration of calcium which is present in the ionic form only and not in the un-dissociated $Ca(NO_3)_2$ form. Therefore prior to the estimation of the material balance of calcium by EDTA titration, it is necessary to predict the percentage dissociation of $Ca(NO_3)_2$ in the reaction mixture. Extent of dissociation of oxalic acid and calcium nitrate in the reaction mixture has been estimated as follow:

Dissociation of oxalic acid and nitric acid (formed in the system) takes place as follow:

Dissociation constant (K_a) of nitric acid is given below (Ansari & Manchanda, 2007)



Dissociation constants (K_a) of oxalic acid are given below (Logan, 1998.)



Dissociation constant of nitric acid is significantly higher than that of oxalic acid, being the stronger acid of the two. As nitric acid dissociates into hydrogen and nitrate ion, it might affect the dissociation of weak oxalic acid due to common ion effect imparted by hydrogen ions and slows down the dissociation of oxalic acid and hence the rate of the main ion-exchange reaction of nitrate to oxalate get reduces. It may also limit the dissociation of calcium nitrate, due to the common ion effect imparted by nitrate ions.

As the nitric acid dissociates completely, the hydrogen ions have to be present in the form of H^+ , $HC_2O_4^-$ and $H_2C_2O_4$. From the experimental studies it was observed that pH of the reaction mixture remains constant i.e. 0.62 after 15 minutes. From these experimental results it was observed that the concentration of hydrogen ions estimated from the obtained experimental pH was the same as the concentration of hydrogen ions resulting from the complete dissociation of the total amount of oxalic acid taken into the system. Therefore, it was concluded that total amount of oxalic acid taken into the system was dissociated completely and as the oxalic acid dissociates completely then calcium nitrate also has to be dissociate completely because calcium nitrate is having higher solubility in aqueous media as compared to oxalic acid. Therefore it was concluded that whatever calcium taken into the system is present its oxalate (precipitated form of reaction product) and unreacted part in the form of ions only rather than calcium nitrate. Therefore, EDTA method is suitable for the estimation of the concentration of entire residual unreacted calcium present in this system. Reactants taken into the system were dissociated completely because, as the reaction proceeds, oxalate and calcium ions get consumed over a period of time and product get precipitated out.

From this study it is observed that as the excess amount of oxalic acid increases then the percentage conversion also increases. From figure-4, it is cleared that 40-50% (by wt) of excess oxalic acid is optimum for achieving 97-98% conversion of calcium nitrate to calcium oxalate over the reaction period of 15 minutes and hence the material balance established on the basis of obtained yield of calcium oxalate monohydrate has been validated by measuring the concentration of unreacted calcium ions in the reaction mixture through EDTA titration.

4.3 Reaction Kinetics

Limiting reactant between calcium nitrate and oxalic acid is calcium nitrate and therefore maximum conversion of calcium nitrate to calcium oxalate was desired. From the kinetic study it has been observed that excess amount of oxalic acid results into the higher conversion as shown in Figure-4 where the X-axis indicates only the serial number of the experiment and Y-axis indicates the % conversion and % amount of excess oxalic acid taken into the system. From the results reported in Table-2 it has been observed that 50% of excess amount of oxalic acid by weight is optimum for carrying out 97-98% conversion within initial 15 minutes as stated earlier and hence the study was focused on understanding the kinetics of the reaction over the reaction period of initial 15 minutes. The kinetics of the reaction during initial 15 minutes, at 50% (by wt.) excess amount of oxalic acid was estimated and has been shown in Figure-5. During this study, a sample was taken periodically and analyzed for its un-reacted calcium content to estimate the extent of conversion using EDTA titration.

From figure-5, it was cleared that the reaction takes place in two stages. In the first stage, 75% conversion is taking place within initial 1st 10 seconds (which is a typical macro mixing time in the experimental set-up used) and remaining 25% gets completed in further 900 seconds and it is considered as 2nd stage. The rate of the reaction in 2nd stage is substantially lower as compared to the 1st stage; possibly due to the dissociation and equilibrium limitations as discussed earlier and therefore it is considered as the rate controlling/limiting step. The plausible reasoning behind of getting such a type of typical reaction kinetics has been discussed as follow.

As the macro and micro mixing of the reactants continues, the dissociation of calcium nitrate and oxalic acid takes place and collisions between calcium and oxalate ions occurs (micro mixing or molecular mixing as a result of agitation) and results into the formation of calcium oxalate instantaneously. Thus, assuming dissociation reaction is spontaneous, the overall reaction is initially controlled by the mixing on molecular level. As 75% of conversion is achieved in the initial 10 seconds, the concentration of the reactants goes down instantly and hence the effective collision frequency (responsible for the reaction) between the un-reacted reactants gets also reduced and the reaction was controlled only by molecular or micro mixing. The second reason is that HNO_3 formed may also retard the dissociation of weak un-dissociated oxalic acid which further reduces the rate of the reaction. Therefore, the rate of the reaction reduces after first 10 seconds and then it remains almost same over the reaction period of 900 seconds or 15 minutes as shown in Figure-5. The rate of the reaction $\frac{-dC_A}{dt}$ in the 2nd stage (after the initial 10 seconds) has been estimated as shown in Figure-5 and its estimated value is $2.33 \times 10^{-8} \text{ gmol/m}^3 \text{ sec}$, with respect to calcium nitrate which almost remains constant till the completion of the reaction at the speed of agitation level equal to or above 350 RPM for the set-up under the consideration.

5. DESIGNING OF THE PROCESS HARDWARE FOR THE CONTINUOUS PRODUCTION OF CALCIUM OXALATE:

Final optimum operating parameters such as excess of oxalic acid needed, reaction kinetics were obtained from the preliminary studies and those are useful to fulfil the requirements for designing the process capable for carrying out the reactive precipitation between calcium nitrate and oxalic acid as per the requirements.

The calcium nitrate should be converted completely to its oxalate otherwise it leads to a minimum loss of strategic material, (calcium nitrate in this case) in the discarded stream. The novel way of carrying out the reaction within minimum volume and with complete conversion has been proposed and designed by considering all the above discussed aspects of the reaction kinetics and equilibrium limitations going to establish in the dissociation of reactants.

As shown in Figure-6, the reactor system consists of mixing section and is followed by a continuous solid removal section. Mixing section consists of two CSTRs (Continuous Stirred Tank Reactor) and one static mixer. 1st small CSTR is followed by a static mixer and a static mixer is followed by 2nd large CSTR. Designing of the overall reactor configuration has been done in order to obtain the solid particle product (monohydrate form of calcium oxalate) with complete conversion of the reactants (calcium nitrate in this case). Mixing section was designed in order to carry out the maximum conversion with agglomeration of particles to achieve the particle size in the required range while the continuous thickener was designed to carry out the reaction to completion and concentrate the slurry so as to reduce the subsequent load on the filtration and drying operations. The concentration of calcium nitrate has been chosen on the basis of concentration of metal ions generally going to be present in the waste streams generating from chemical or nuclear industries and it is in the range of 0.1M and the concentration of oxalic acid of 0.5M was chosen in order to maintain the atomic ratio of hydrogen to nuclear element below the criticality limit if the process hardware implemented as such for treating out the waste generating especially from nuclear industries. At this concentration level of reactants, 40-50% of excess oxalic acid by weight was optimum for carrying out complete conversion of calcium nitrate to its oxalated over the reaction period of 15 minutes as already studied in the reaction kinetics. Therefore the combined flow rate of the reactants of $4.23 \times 10^{-5} \text{ m}^3/\text{sec}$ consisting of 0.1M of aq. Calcium nitrate and 0.5M of aq. Oxalic acid (50% excess by wt) is sufficient for the production of 52 kg of calcium oxalate per day on a continuous basis by considering the plant duty of 24 hrs. The

residence time of solid in each of the section and sizing of the section has been decided on the basis of solid hold-up of calcium oxalate in either of the sections should not reach the criticality limit if the system is implemented as such for treating out the radioactive waste generating from the Purex process in nuclear industries. The system designed by knowing the volumetric flow rates of the reactants in the present work consists of two sections, as mixing section is followed by solid removal section having the average residence time in each of the section is of 600 seconds and it is decided on the basis that the maximum accumulated mass of calcium in each of the section should be 20 to 25 % of the 0.5 kg (the typical critical mass of Pu-239). The hold-up of the solid mass (calcium oxalate) in the mixing section and continuous thickener has been estimated on the basis of residence time of solid inside the system and it is 0.360 kg in each of the section containing calcium of 0.1125 kg only. The volume of each section has been estimated by knowing the volumetric flow rate and the mean residence time. Geometrical parameters of each section has been decided on the basis of sizing of the reactor, reactor shape and areal density.

5.1 Designing of the Mixing Section

Mixing part consists of two CSTRs in series as 1st small one is followed by 2nd large one. This typical type of arrangement of reactors is necessary because as the reaction proceeds reaction mixture becomes more and more acidic due to the formation of the reaction byproduct nitric acid which hinders the further dissociation of the fresh oxalic acid being weak of the acids coming from feed and hence the rate of the reaction in first stage reduces. Therefore it is necessary to pre-mix the feed of calcium nitrate and oxalic acid in order to carry out at least 75% conversion in the 1st stage itself and it is carried out in the first small CSTR having a much smaller residence time of 10 seconds and online static mixer as shown in Figure-6, before it is fed to the 2nd large CSTR (having the higher concentration of nitric acid) providing the needed residence time for carrying out the reaction in the 2nd stage and to agglomerate the particle size to proper range.

With the information of mean residence time of the Mixing section and the volumetric flow rate, the volumetric capacity of mixing section has been estimated and is of 0.0254 m³ (600 seconds of mean residence time). Material balance across the mixing section has been established with the knowledge of volumetric capacity, rate of the reaction and flow rate of the reactants. Mixing section consists of two CSTR in series and it is assumed that both CSTRs present in the mixing section are acting as ideal reactors. Material balance across these two CSTRs has been established. Overall 89% conversion is expected across the mixing section. Out of this 89% conversion, 75% is expected across the 1st small CSTR during the 1st stage and remaining 14% is expected across the 2nd CSTR during the 2nd stage.

5.1.2 Scale-up Criteria of Mixing Section

The scale-up criterion used was that of power dissipation per unit volume, which was kept constant. Therefore, power dissipation (dissipated by agitation) (watts/m³) per unit volume for batch reactor (used in the preliminary mixing studies) and CSTR should be the same.

Standard geometry of stirred tank reactor has been considered for the fabrication of CSTRs (McCabe, et al., 1993). Both small and large CSTR have been fabricated having the volume of 0.00423 m³ (mean residence time of 10 seconds) and 0.0254 m³ respectively. The agitation level in the large CSTR of scaled up system has been estimated and it is around of 146 RPM. This speed of agitation should be sufficient to keep all the particles in suspension. The largest particle size achieved is of the order of 70µm. Therefore, the speed of agitation should be sufficient to keep the particles having the size of 70µm in suspension. The critical speed for suspension to keep the particles of largest size (70µm) in

suspension has been estimated using Zwetering's Correlation (McCabe, et al., 1993) and it is about 80 RPM which is much lower than the operating speed of agitation of 146 RPM estimated from the scale up criteria.

6. CHARACTERIZATION OF REACTOR SYSTEM

Residence time distribution (RTD) measurement was carried out to characterize the mixing section in order to know the deviation from ideality and to predict the conversion occurring across the mixing section and solid removal section. Residence time distribution (RTD) study has been used to characterize and model the mixing part of reactor system and pulse input was used for this study. As discussed previously mixing part consists of 1st CSTR followed by a static mixer and static mixer is followed by 2nd CSTR. Static mixer has been modelled as a plug flow reactor (PFR). Therefore the resulting system has been shown schematically in Figure-7. It was assumed that a known quantity of tracer injected in the 1st CSTR and its concentration at the exit of 2nd CSTR has been predicted using the RTD models and validated experimentally.

Development of RTD models for the prediction of tracer concentration at the exit of 2nd CSTR:

Tracer injected in the 1st CSTR starts entering the 2nd CSTR after time τ_p

Where, $\tau_p = \text{mean residence time of the static mixer}$

Therefore, material balance of tracer across the 2nd CSTR for time $t < \tau_p$ is given by

$$FC = 0; \quad \text{for } t < \tau_p \quad (7)$$

Where, F is the volumetric flow rate (m^3/s) and C is the tracer concentration at the exit of 2nd CSTR (kg/m^3).

Material balance of tracer across the 2nd CSTR for time $t \geq \tau_p$ is given by

$$FC_i = FC + V_2 \frac{dC}{dt}; \quad \text{for } t \geq \tau_p \quad (8)$$

Where, V_2 is the volume of the second CSTR.

By using the RTD model, equation (8) can be written as follow

$$E(t)M = FC + V_2 \frac{dC}{dt}; \quad \text{for } t \geq \tau_p \quad (9)$$

Where, M is the total mass of the tracer injected in the 1st CSTR and $E(t)$ is the exit age distribution at the outlet of static mixer (s^{-1}). $E(t)$ is the fraction of the total amount of tracer injected in the system coming out of the system per unit time. 1st CSTR is followed by a static mixer. Therefore, the $E(t)$ is given by (Fogler., 2011)

$$E(t) = \frac{e^{-\frac{(t-\tau_p)}{\tau_{s1}}}}{\tau_{s1}} \quad (10)$$

Following equation is obtained by substituting the equation (10) in equation (9)

$$\frac{e^{-\frac{(t-\tau_p)}{\tau_{s1}}}}{\tau_{s1}} M = FC + V_2 \frac{dC}{dt}; \quad \text{for } t \geq \tau_p \quad (11)$$

Equation (11) can be solved numerically as follow

$$\frac{e^{-\frac{(t-\tau_p)}{\tau_{s1}}}}{\tau_{s1}} M = FC_{old} + V_2 \frac{(C_{new}-C_{old})}{\Delta t}; \text{ for } t \geq \tau_p \quad (12)$$

Above model is valid only for the period of first four minutes because more than 99% of total amount of tracer injected in the inlet of 1st CSTR is released completely in the 2nd CSTR within first four minutes. Therefore, material balance of the tracer across the 2nd CSTR for time $t > 4$ minutes is given by

$$FC + V_2 \frac{dC}{dt} = 0; \text{ for } t > 240 \text{ sec.} \quad (13)$$

$$\therefore FC_{old} + V_2 \frac{(C_{new}-C_{old})}{\Delta t} = 0; \text{ for } t > 240 \text{ sec} \quad (14)$$

Above models are solved by Euler's method by taking the time interval of one second (Bird, 2010.). The experimental variation in the tracer concentrations at the exit of 2nd CSTR with respect to time has been shown graphically in Figure-8 and compared with the predicted results. From this study it has been observed that there is more than 99% similarity between the predicted and experimentally obtained results which finally concludes that the real system behaves almost ideally.

7. DESIGNING OF SOLID REMOVAL SECTION

Continuous thickener has been designed to remove the solid product continuously and to carry out the residual conversion of un-reacted reactants coming out from the mixing section. Batch sedimentation experiment has been carried out to estimate the settling velocity of the solid mass and its estimated value is 7.9×10^{-4} m/s. This is necessary as the upward clear liquid velocity going towards the overflow nozzle position must be substantially less than the settling velocity to prevent any particle carryover. The input concentration of slurry (kg of precipitated solid mass per m³ of liquid) going to the thickener is 11.23 kg/m³ and it has to increase up to 18.52 kg/m³. Input flow rate is of 4.23×10^{-5} m³/s. By knowing all these parameters, material balance across the continuous thickener has been carried out and on the basis of that the cross sectional area of thickener needed for the required extent of separation has been estimated from the following relation obtained from the mass balance across the continuous thickener.

$$A = \frac{(Q_i \times C_{in} \times (\frac{1}{C_{in}} - \frac{1}{C_u}))}{V_i} \quad (15)$$

Where, Q_i (m³/s) is the inlet volumetric flow rate fed to the continuous thickener, C_{in} and C_u (kg/m³) are the concentrations of calcium oxalate monohydrate in the inlet stream and underflow of the continuous thickener respectively. V_i (m/s) is the settling velocity of solid calcium oxalate monohydrate.

By knowing the area, the diameter has been estimated and it is 0.15m. The volume of a continuous thickener has been estimated on the basis of complete conversion criteria of the un-reacted reactants coming out from the mixing part and it is of 0.015 m³. As a safety, 100% large diameter has been provided during the fabrication of a continuous thickener to ensure complete settling of the solid mass and to obtain clear liquid at the overflow. Thus, a continuous thickener having the diameter of 0.3m and already decided volumetric capacity (on the basis of criticality limit) of 0.0254 m³ has been fabricated.

8. COMPARISON OF THE DESIGNED PROCESS HARDWARE WITH THE SYSTEM CONTAINING THE FISSIONABLE ELEMENT THROUGH THE CRITICALITY POINT OF VIEW.

The designed continuous process hardware should be safe if it is implemented as such for treating out the waste generating from the Purex process in nuclear industries. A critical mass is the least amount of fissile material needed for a sustained nuclear chain reactions and it depends on the number of parameters like accumulated mass of the nuclear element in the equipment, areal density or the atomic ratio of hydrogen to nuclear element. Therefore, it is necessary to check out first whether the designed configuration is safe or not before going to implement in nuclear industries by taken the system containing the nuclear element like Pu-239. Subcriticality limits for aqueous solutions of Pu-239 depends on the different parameters like accumulated mass of plutonium in the system, areal density or hydrogen to plutonium atomic ratio has been noted down in Table-3 (Clark, 1981). If any one of these parameters is lower than the subcriticality limit then system configuration appears to be safe. In this research work efforts are made to maintain all these three parameters below the subcriticality limits. The first controlled parameter through the criticality point of view is the accumulated mass of plutonium in any part of the process configuration has been maintained 75-80% less than the subcriticality limit of 0.5 kg. The second controlled parameter is the areal density and it is for the designed process configuration is 0.33 kg/m^2 which is 85-90 % less than the subcriticality limit of 2.5 kg/m^2 as noted down in Table 3. The third controlled parameter is the atomic ratio of hydrogen to Pu-239 of around 2800-2900 which is lower as compared to the subcriticality limit of 3600 as noted down in Table 3. Therefore, finally the conclusion is made and it is that the continuous process hardware designed in the present research work appears to be safe if it is implemented for treating out the waste of Purex process containing the nuclear element like Pu-239.

9. PREDICTION OF CONVERSION

9.1 Prediction of Conversion Across the Mixing Section via RTD Models

Mixing part consists of two CSTRs in series. From the characterization of mixing part it was observed that it has 99% of ideal approach. Therefore, segregation model has been used to predict the conversion occurring across the mixing section (Fogler., 2011). If the material injected in the CSTR starts to come out from time $t=0$ and continues up to $t=\infty$. Then, the overall conversion obtained in the CSTR is given by

$$X = \int_0^{\infty} X(t)E(t)dt \quad (16)$$

The predicted conversion across the mixing part of the reactor system is 86.9% (75% in the 1st CSTR during the 1st stage and remaining of 86.9% in the 2nd CSTR during the 2nd stage) and experimentally obtained conversion is 89% and thereby validating the model.

9.2. Prediction of the conversion across the continuous solid removal section via diffusion model:

Continuous thickener acts like a tubular flow reactor operating in a laminar flow regime. Therefore, conversion occurring across it has been predicted using diffusion model as follow (Fogler., 2011).

$$\frac{C_{A0}}{Pe_r} \frac{d^2 \psi}{d\lambda^2} - C_{A0} \frac{d\psi}{d\lambda} + r_A \tau = 0 \quad (17)$$

Where,

Pe_r is the Peclet number, C_{A0} is the concentration of calcium nitrate in the stream fed to the continuous thickener (gmol/m^3), $-r_A$ is the rate of reaction ($\text{gmol/m}^3\text{s}$), Ψ is C_A/C_{A0} , C_A is the concentration of calcium nitrate in the thickener at any distance (Y) from the bottom of thickener and λ is Y/H , where H is the total height of continuous thickener.

Peclet number has been estimated from the RTD study and it is equal to 4. The values of ψ at different values of λ have been estimated and it is 0 at λ equal to 0.31, i.e. 31% of total volume of continuous thickener is sufficient for carrying out complete residual conversion of unreacted reactants coming out from the mixing section.

10. CONCLUSIONS

The reaction of calcium nitrate with oxalic acid in aqueous media results into the formation of monohydrate of calcium oxalate under the reaction conditions presented in this work. 50% (by wt) of excess amount of oxalic acid appears to be optimum for carrying out complete conversion of calcium nitrate to calcium oxalate over the reaction period of 15 minutes in a continuous manner. From the kinetic study it is observed that reaction takes place in two with 75% conversion is completed within first 10 seconds (which is a typical macro mixing time in the set-up used) and the balance 25% reaction takes about 900 more seconds and it is considered as a second stage. The rate of reaction in the second stage was found to be $2.33 \times 10^{-8} \text{gmol/m}^3\text{s}$ which is substantially lower than the 1st stage and hence it is the rate controlling step. On the basis of parameters obtained from the preliminary studies; a continuous process hardware capable for the synthesis of calcium oxalate has been designed and validated as per the requirements.

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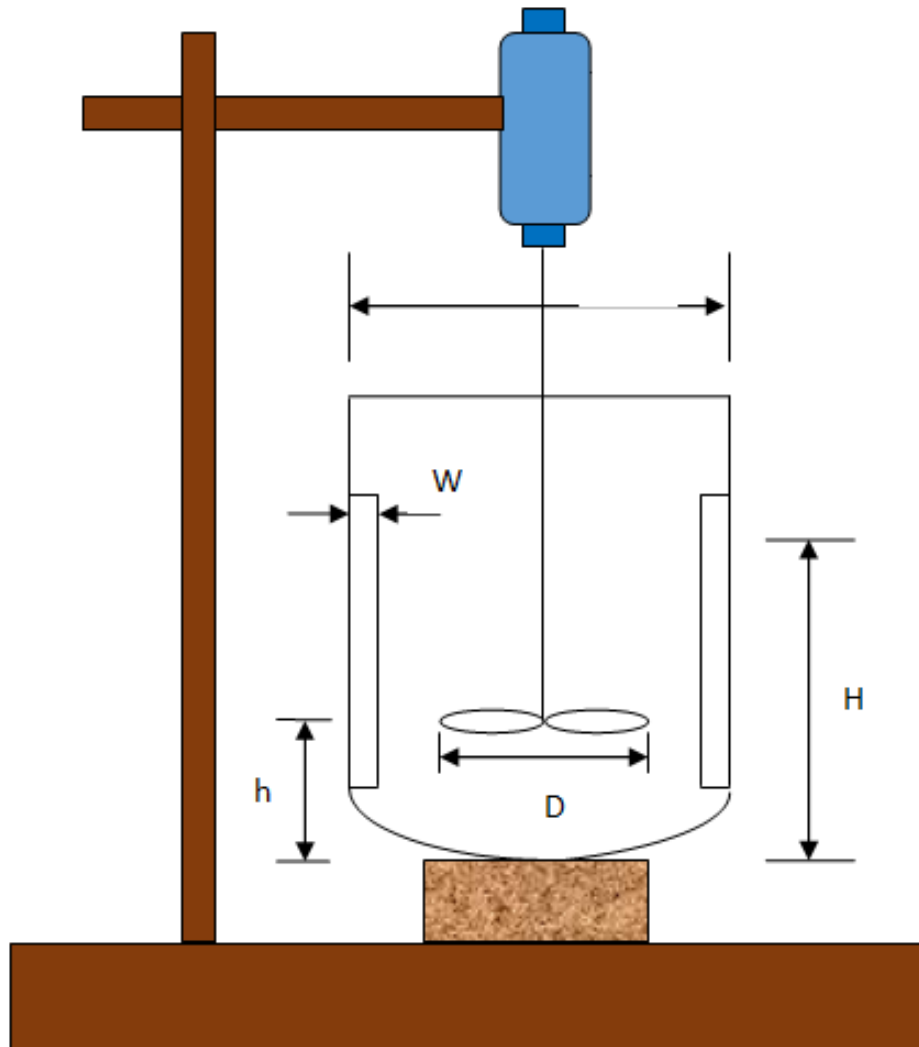


Figure 1: Experimental Set-up for the Synthesis of Hydrated Calcium Oxalate.

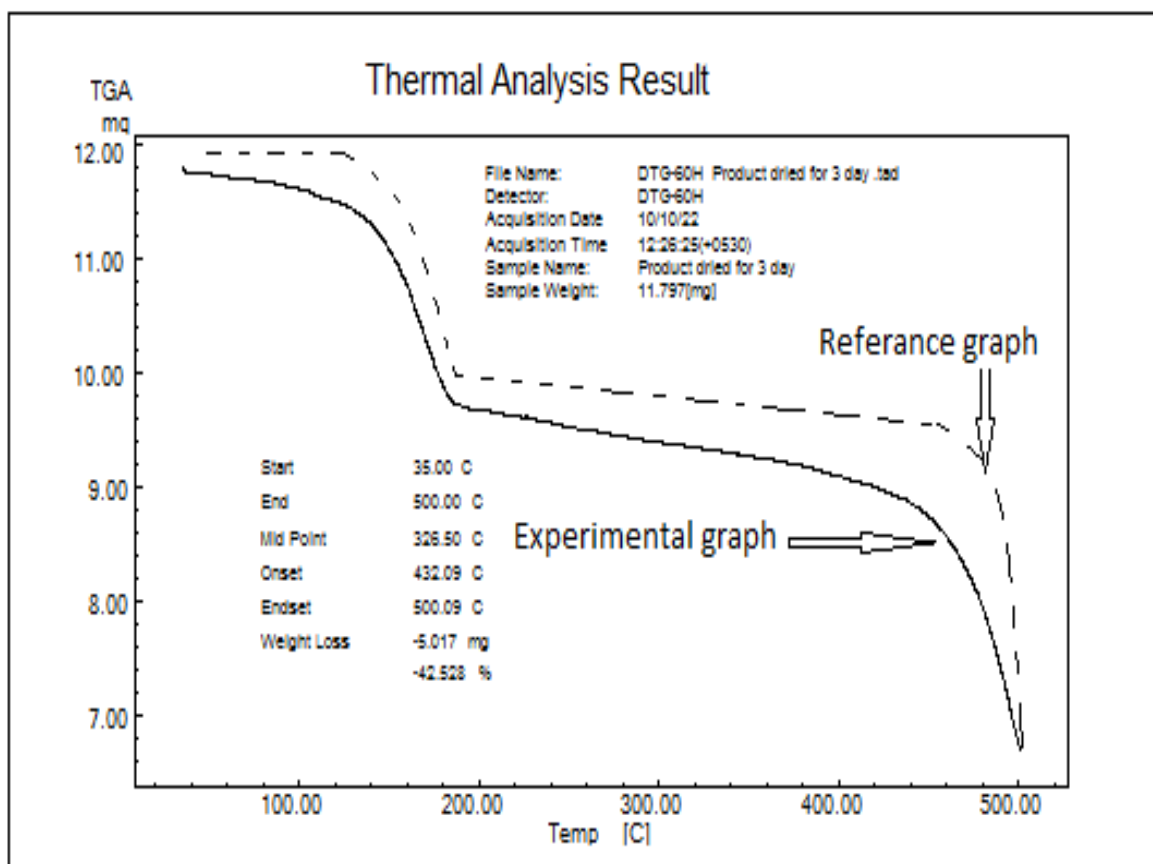


Figure 2: TGA Analysis of Hydrated Calcium Oxalate.

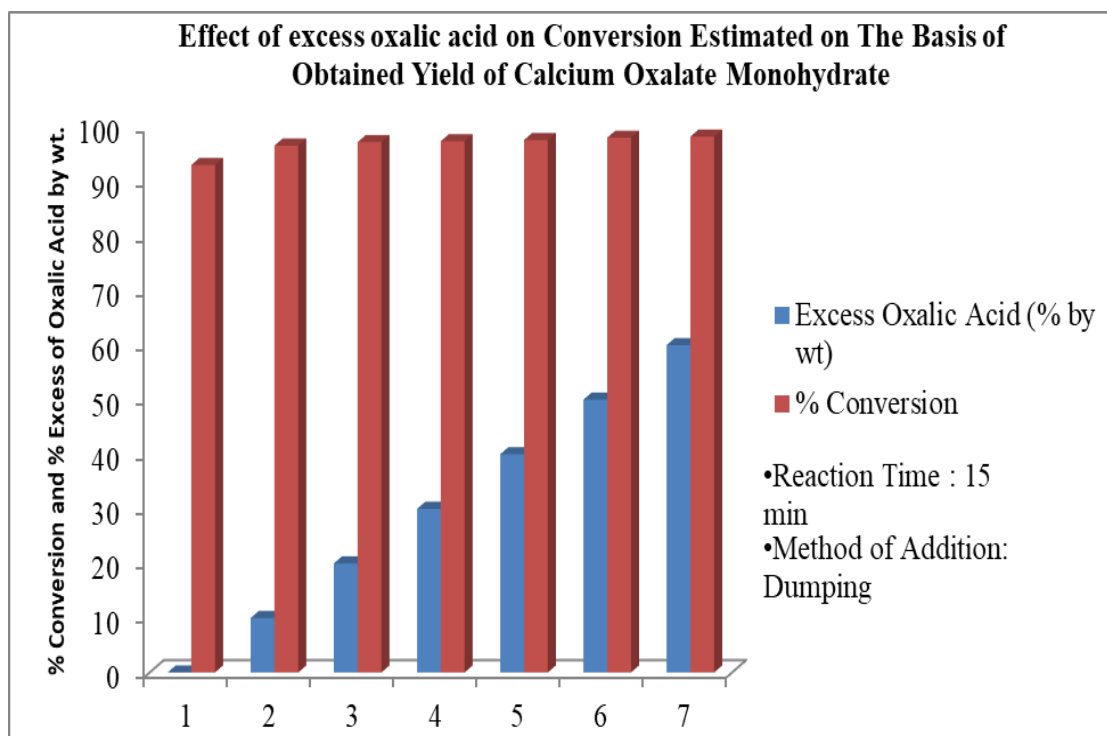


Figure 3: Effect of Excess Oxalic Acid on the Conversion.

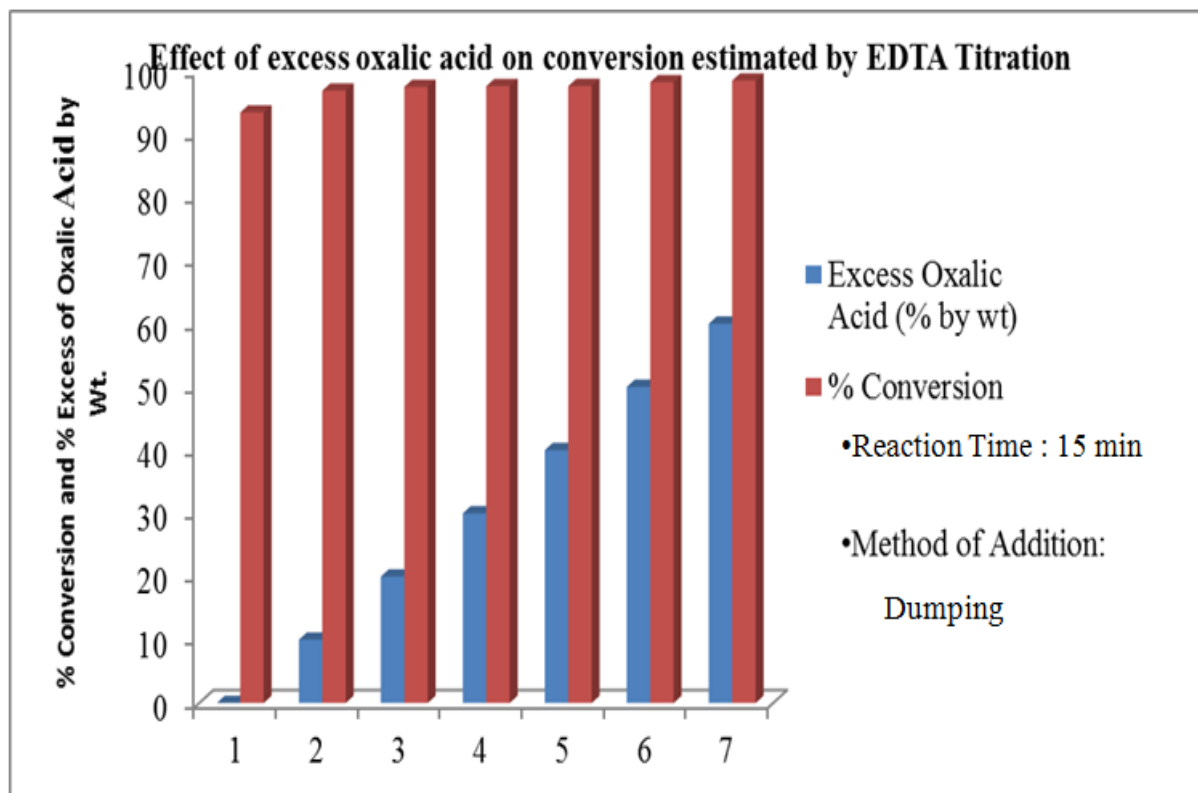


Figure 4: Effect of Excess Oxalic Acid on the Conversion.

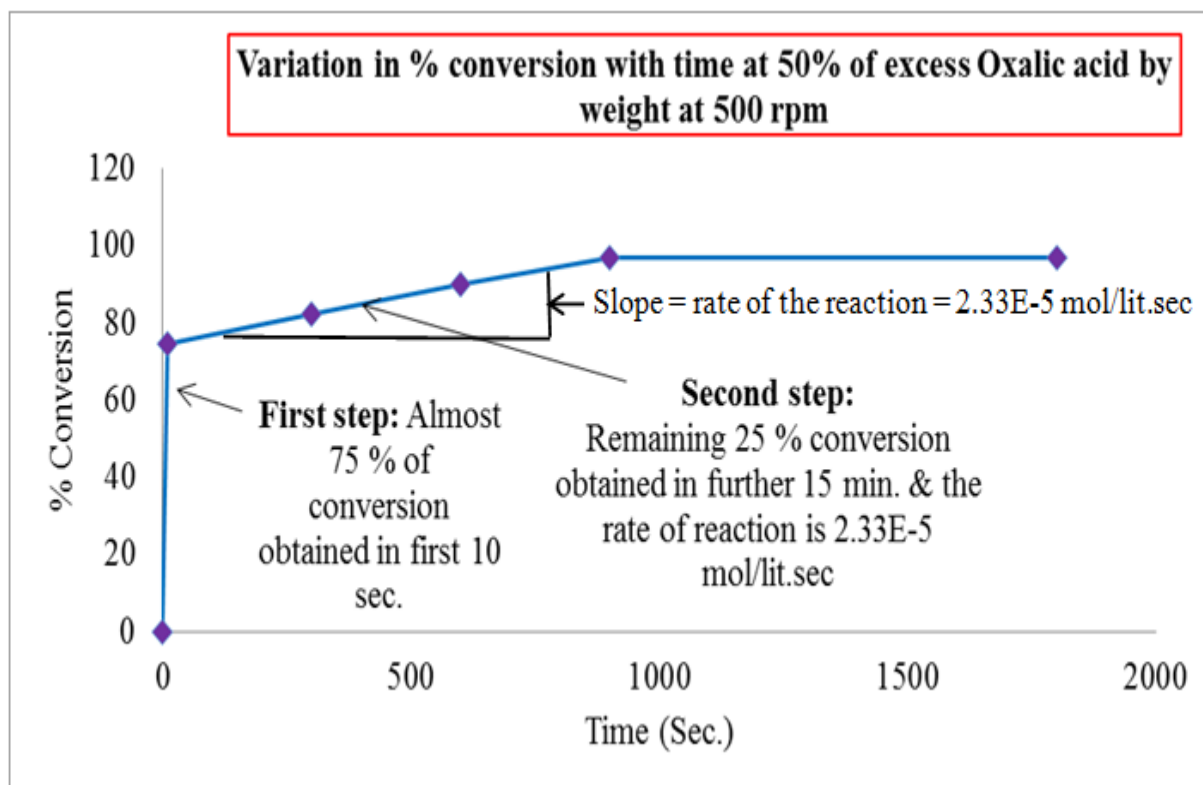


Figure 5: Variation in % Conversion with Time at 50% of Excess Oxalic Acid by Weight.

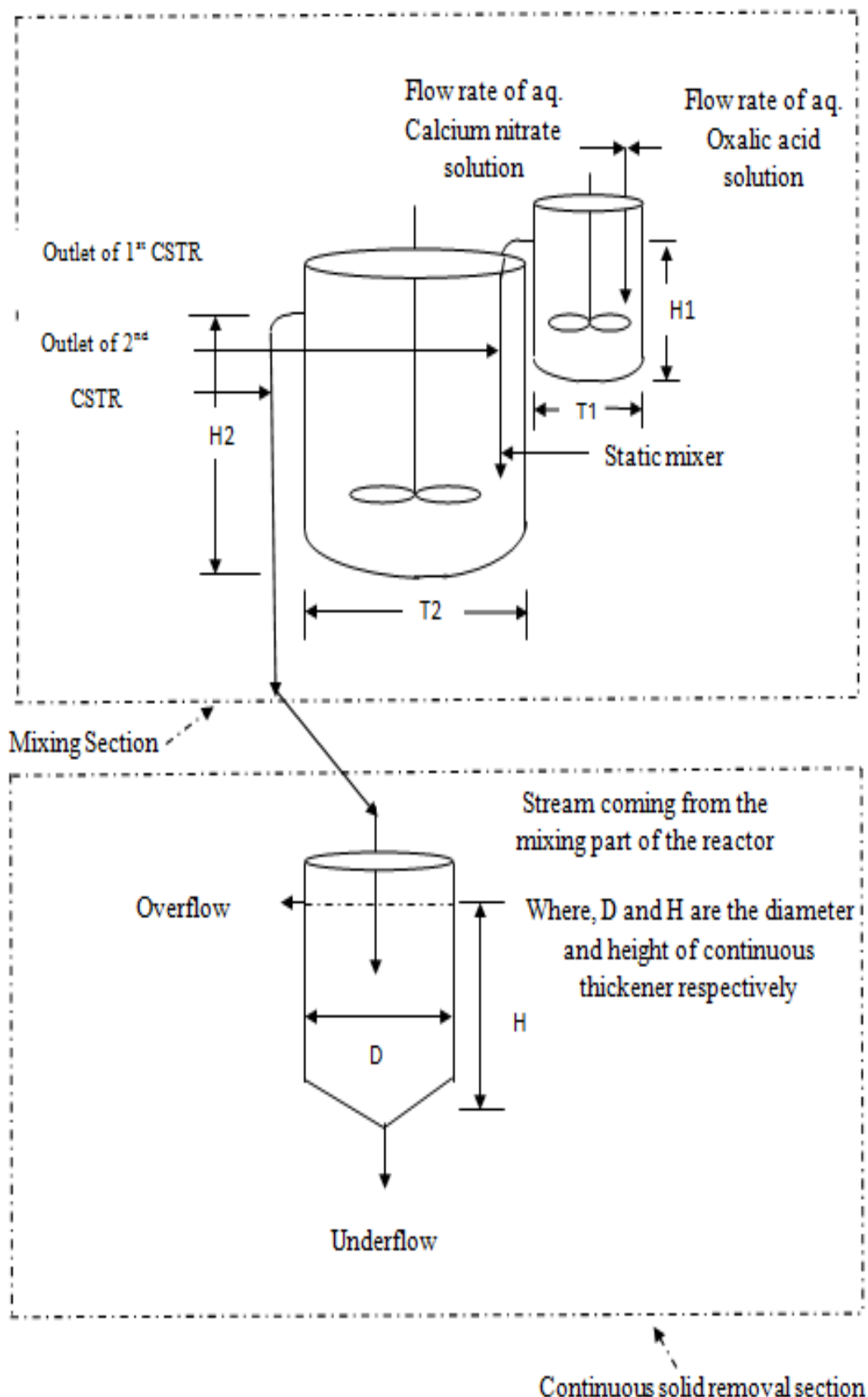


Figure 6: Reactor System for Carrying out Reactive Precipitation between Calcium Nitrate and Oxalic Acid.

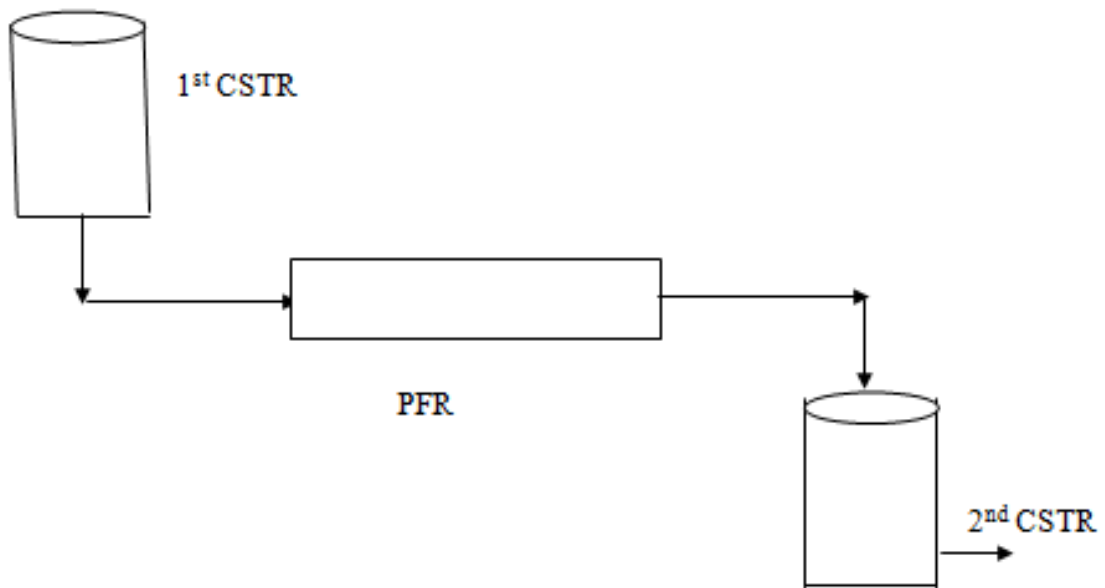


Figure 7: 1st CSTR is followed by PFR and PFR is followed by 2nd CSTR.

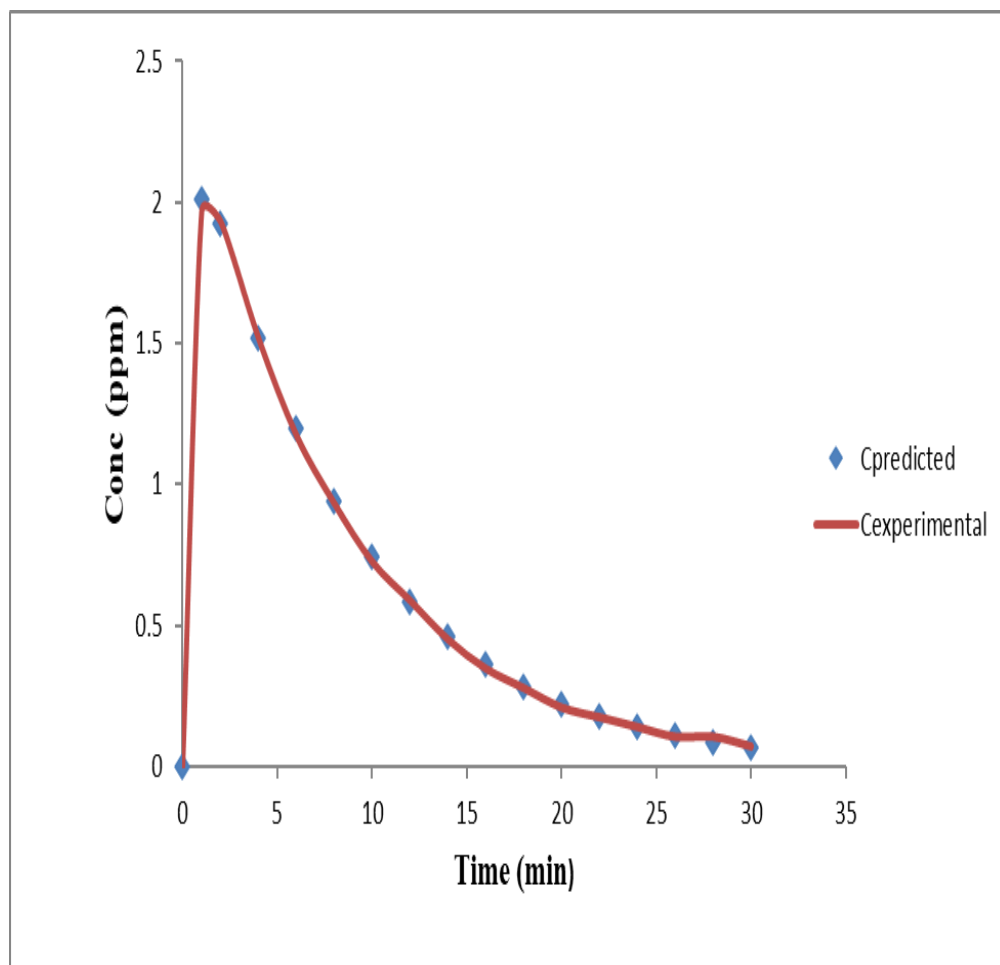


Figure 8: Graphical Representation of Experimental and Predicted Tracer Concentration at the Exit of Mixing Section.

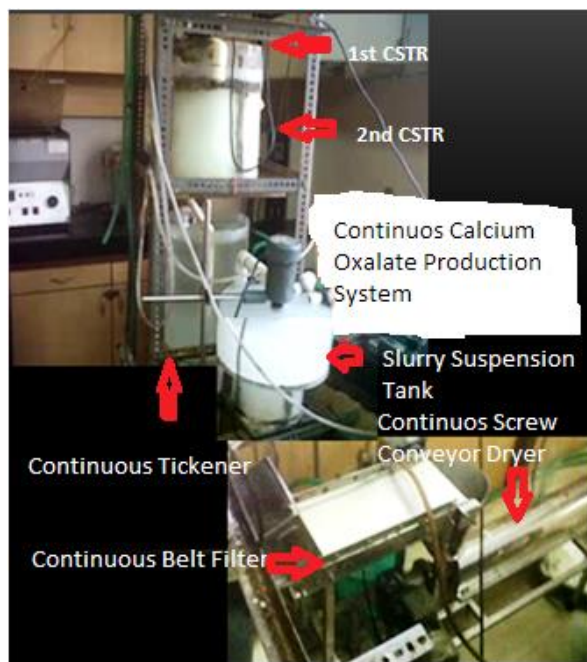


Figure 9: Continuous Calcium Oxalate Production System.

Table 1: Geometric Details of the Batch Experimental set-up.

Diameter of the reactor (T)	115 mm
Height of the reactor (H)	115 mm
Diameter of the stirrer (D)	40 mm
Width of baffle (W)	10 mm
Height of the stirrer from bottom of the reactor (h)	40 mm

Table 2: Complete set of Material Balance of the Reactant Calcium Nitrate

Sr. No.	Concentration of Calcium Nitrate (M)	Concentration of Oxalic Acid (M)	Volume of Calcium Nitrate Taken (ml)	Volume of Oxalic Acid Taken (ml)	Stirring Time (min)	Excess Oxalic Acid (% by vol.)	% Conversion
1	0.1	0.5	500	100	15	0	94.8
2	0.1	0.5	500	110	15	10	96.86
3	0.1	0.5	500	120	15	20	97.45
4	0.1	0.5	500	130	15	30	97.57
5	0.1	0.5	500	140	15	40	98.07
6	0.1	0.5	500	150	15	50	98.19
7	0.1	0.5	500	160	15	60	98.45
8	0.1	0.5	500	170	15	70	98.56

Table 3: Subcritical Limits for Aqueous Systems Containing Plutonium 100% ^{239}Pu

Parameter	Solutions of $\text{Pu}(\text{NO}_3)_4$			
	Standard	HRXN-ANISN	GLASS-ANISN	MGBS-TGAN
Plutonium mass (kg)	0.51	0.489	0.477	0.453
Volume (m^3)	7.7×10^{-3}	7.35×10^{-3}	7.29×10^{-3}	7.16×10^{-3}
H to Pu atomic ratio		3600	3630	3700
Areal density (kg Pu/m^2)	2.5	2.55	2.54	2.45

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Author Contributions

S.G.Shingade and P.D.Gangawane conceived and designed the experiments. S.G.Shingade designed the process hardware. S.G.Shingade fabricated the designed system, characterized, validated experimentally and correlated with the theoretically predicted results. S.G.Shingade and P.D.Gangawane co-wrote the paper. All authors discussed the results and commented on the manuscript.

Competing Interests

The authors declare no competing financial interests.